

Supporting Information

Title: Platinum Particles Supported On Titanium Nitride: An Efficient Electrode Material for the Oxidation of Methanol in Alkaline Media

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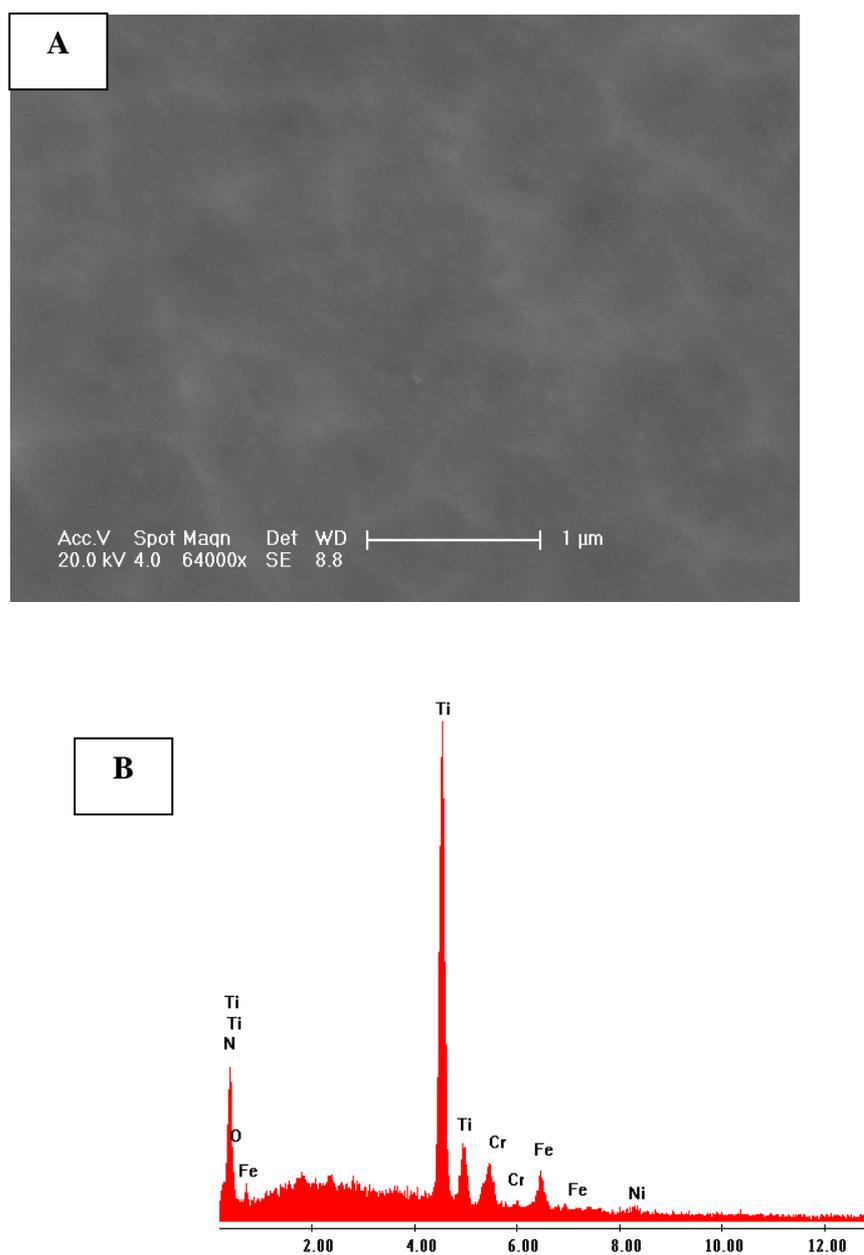


Fig. S1 (A) Scanning electron micrograph of titanium nitride thin film coated on SS-304. (B) EDS pattern of TiN thin film coated on SS-304.

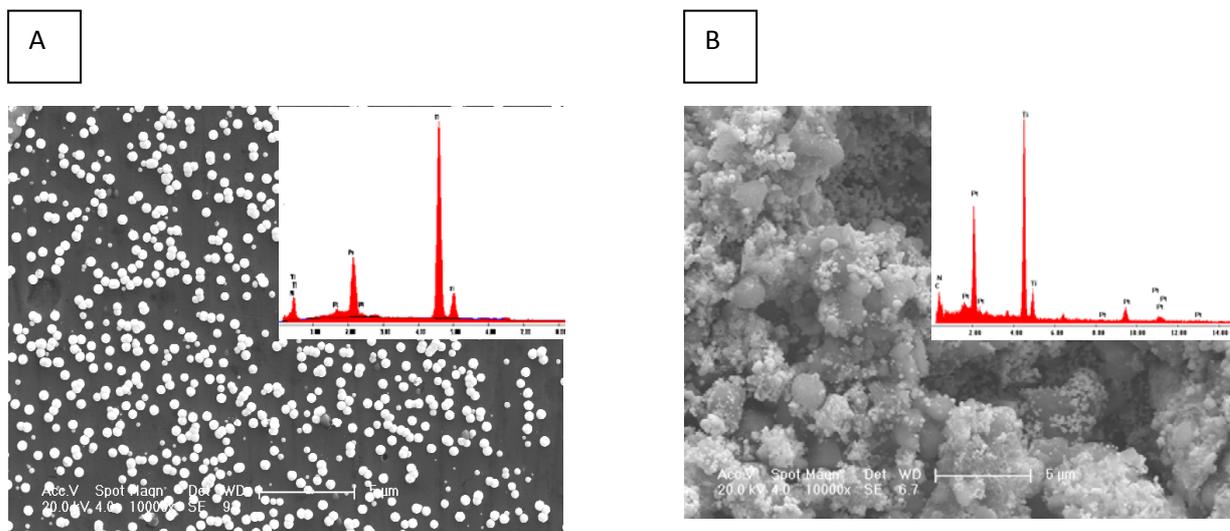


Fig. S2 (A) Scanning electron micrographs of Pt coated titanium nitride (Pt-TiN) film and Pt coated titanium nitride powder (Pt-TiN) (B). Corresponding EDS patterns are also given.

It should be noted that the particle size range of Pt is smaller on the TiN powder than that on TiN film. The magnification and scale bars are the same for both figures (10,000 X and 5 μm). The Pt deposition is carried out by electrochemical method on TiN film and by chemical reduction on TiN powder.

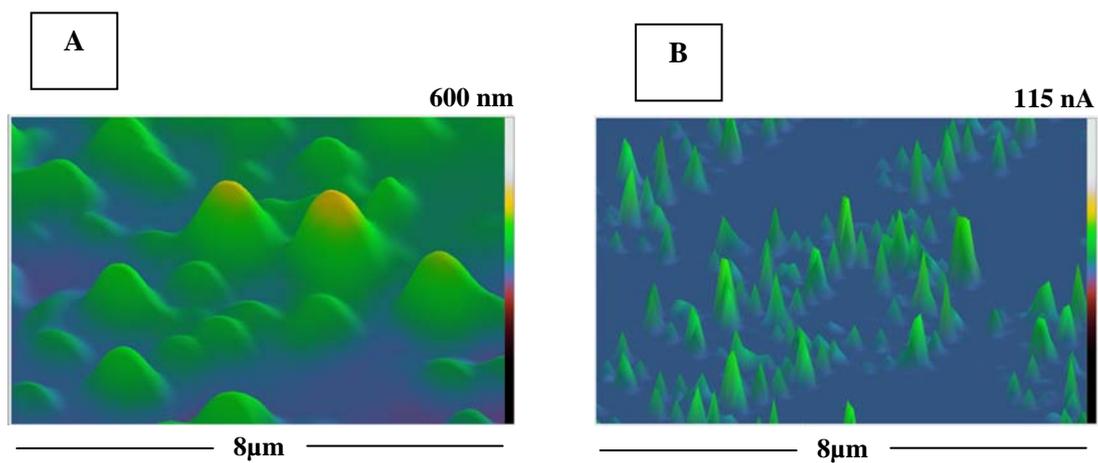


Fig. S3 AFM (A) and the corresponding conductive AFM (B) images of Pt-TiN. The current images recorded at a sample bias of 0.5V with respect to the tip.

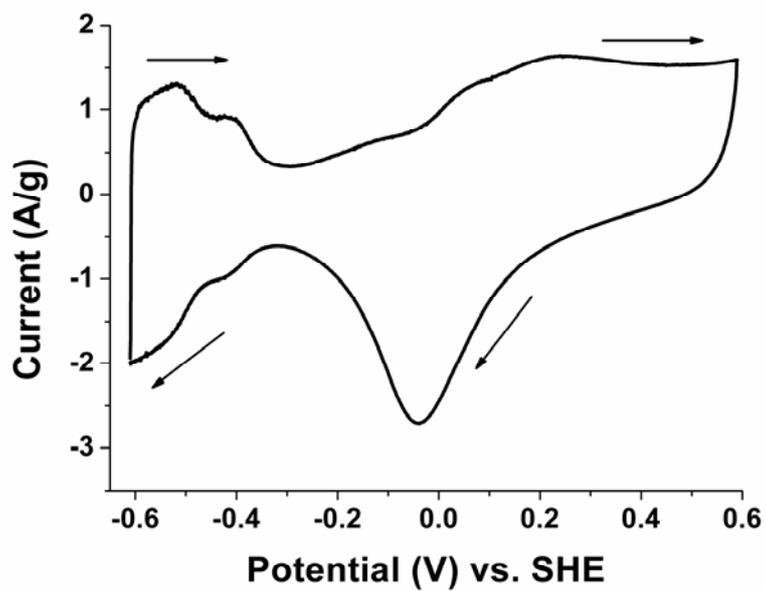


Fig. S4 Cyclic voltammogram of Pt-TiN in 1M KOH at a scan rate of 20 mV/s. Pt loading is 16 μ g (64 μ g/cm²). Geometric area of TiN electrode is 0.25cm².

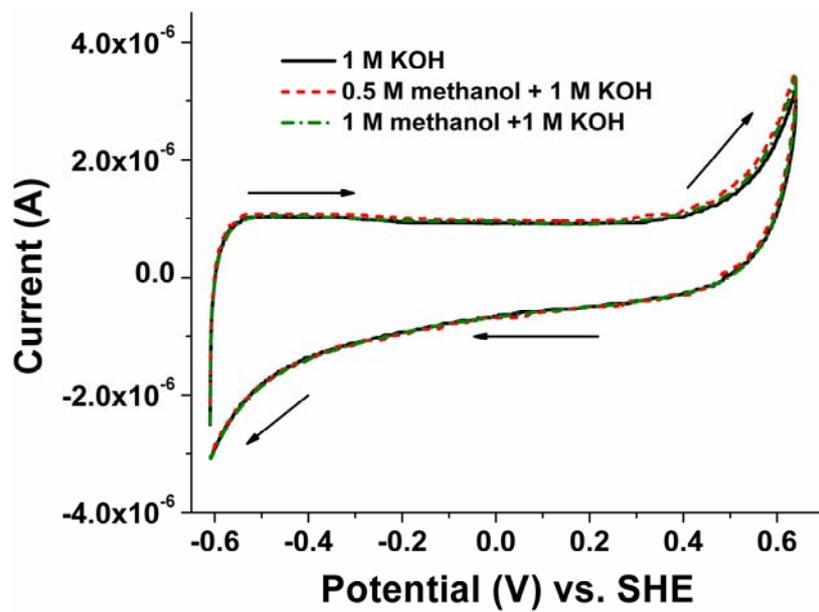


Fig. S5 Voltammogram of bare TiN in 1M KOH (Black line) as a function of methanol concentration.

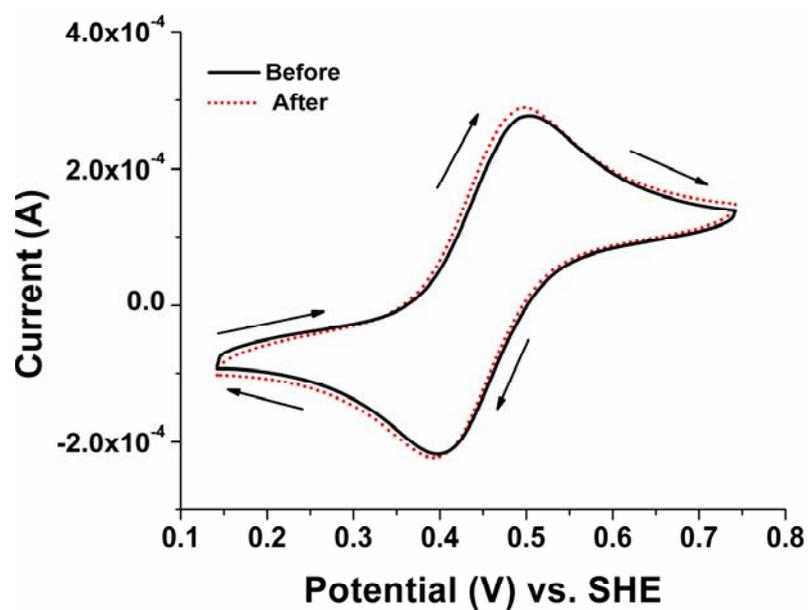


Fig. S6 Voltammograms for 1mM of $[\text{Fe}(\text{CN})_6]^{4-}$ redox couple in 0.1M KCl at 50 mV/s scan rate on Pt-TiN electrode before (solid black line) and after (red dot line) electrochemical oxidation of methanol. Pt loading used is $30 \mu\text{g}/\text{cm}^2$ and the geometric area of the TiN electrode is 0.5 cm^2 .

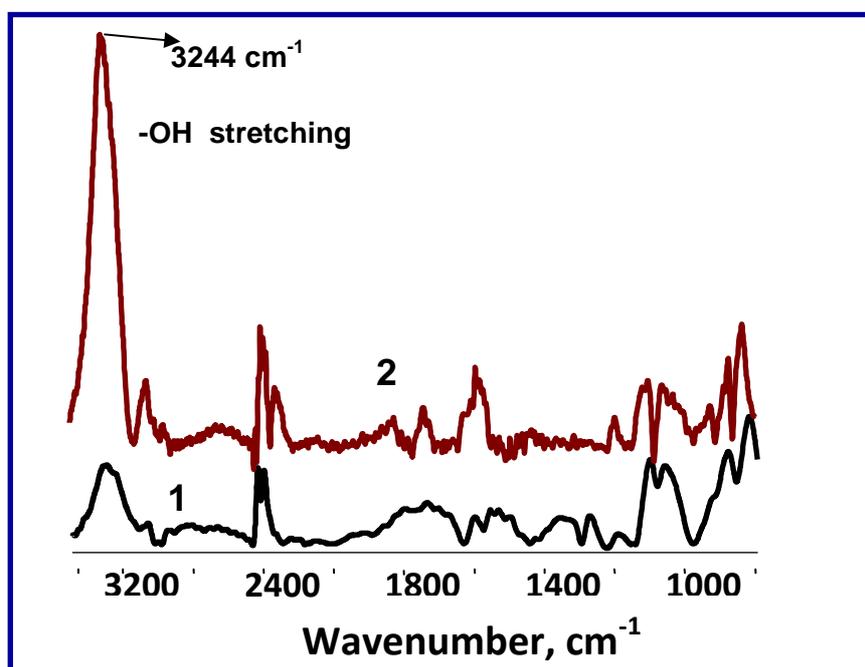


Fig. S7 RAIR spectra of fresh and TiN and the TiN used for the electrooxidation of 0.5M methanol in 1M KOH. The oxidation has been carried out for 10 cycles at 20 mV/sec scan rate.

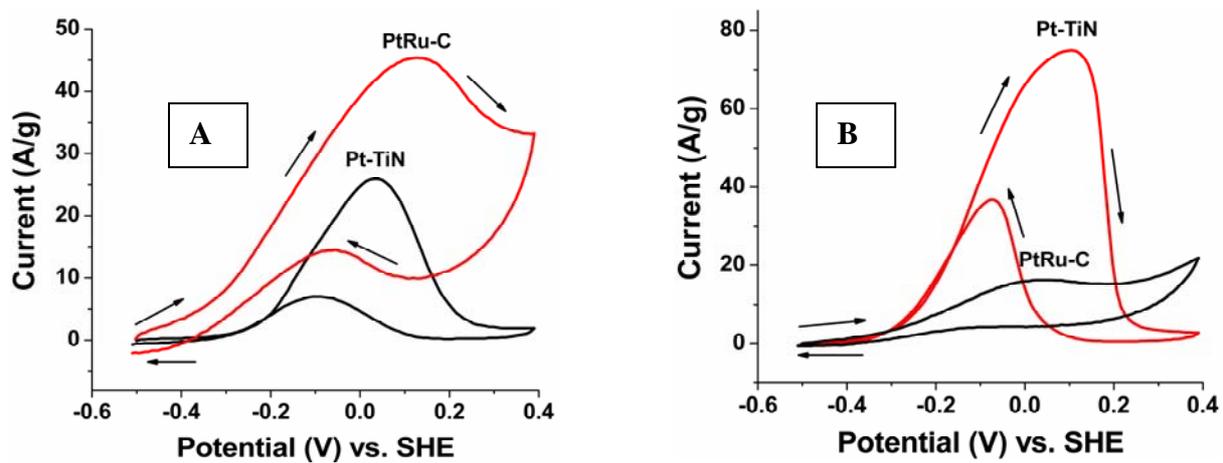


Fig. S8 Cyclic voltammograms of Pt-TiN powder and PtRu in 0.5M methanol in 1M KOH at 20 mV/s. (A) 1st cycle. (B) 50th cycle. Catalyst loading is 1 mg of Pt /cm².

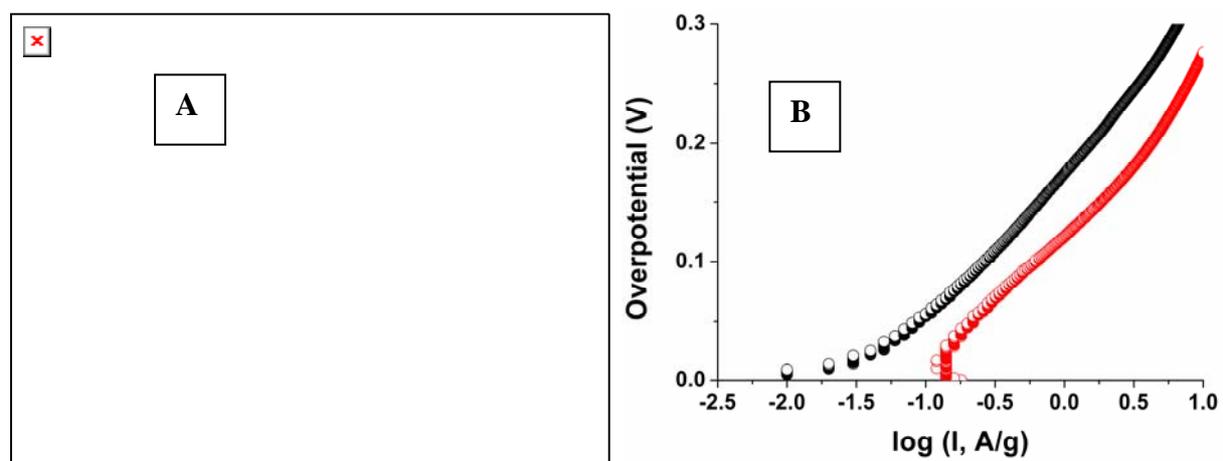


Fig. S9 Tafel plots for (A) PtRu-C and (B) Pt-TiN electrodes in 0.5M methanol + 1 M KOH at 0.5 mV/s. Loading of catalyst is 1mg of Pt /cm². Black and red represents the behaviour of the electrodes before and after cycling respectively. Cycling is carried out between -0.51 to 0.39V vs. SHE for 50 cycles.

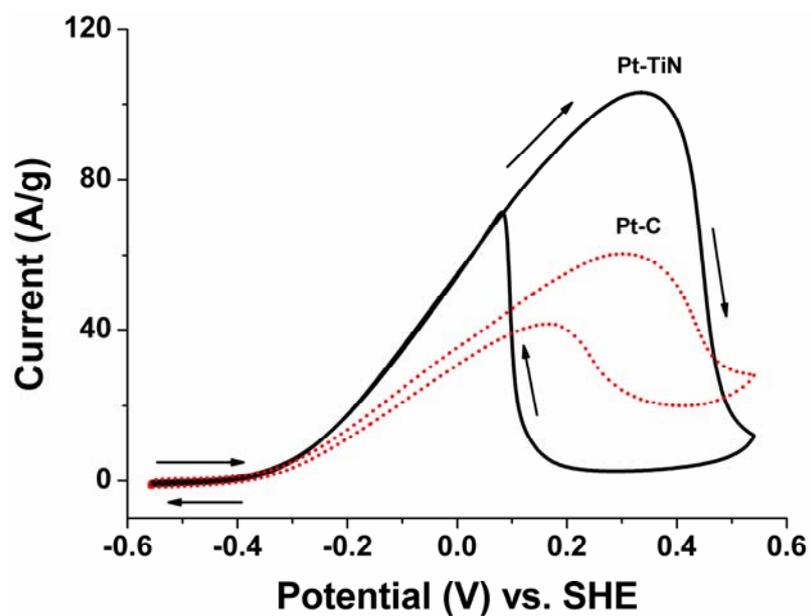


Fig. S10 Voltammograms for the electrooxidation of methanol at Pt-TiN and Pt-C electrodes at 20mV/s. Loading is 1mg of Pt/cm². The electrolyte is 0.5M methanol in 1M KOH.

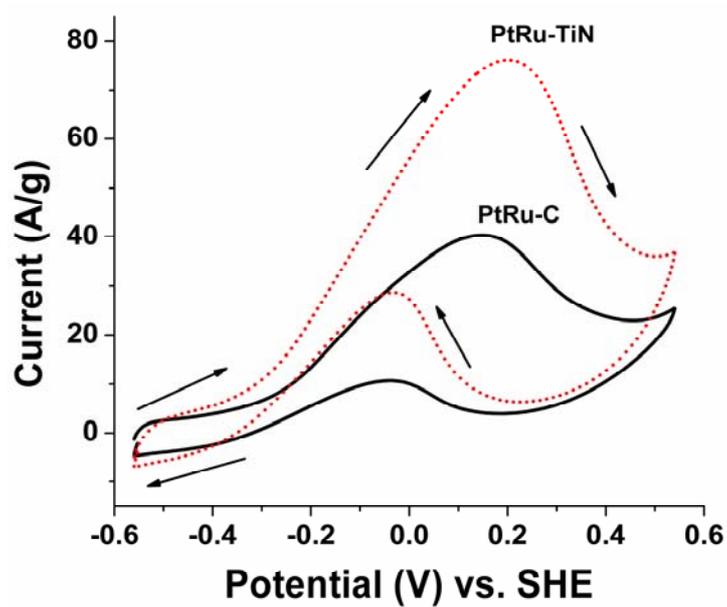


Fig. S11 Voltammograms for the electrooxidation of methanol at PtRu-TiN and PtRu-C electrodes at 20mV/s. Loading is 1 mg of Pt/cm². The electrolyte is 0.5M methanol in 1M KOH.

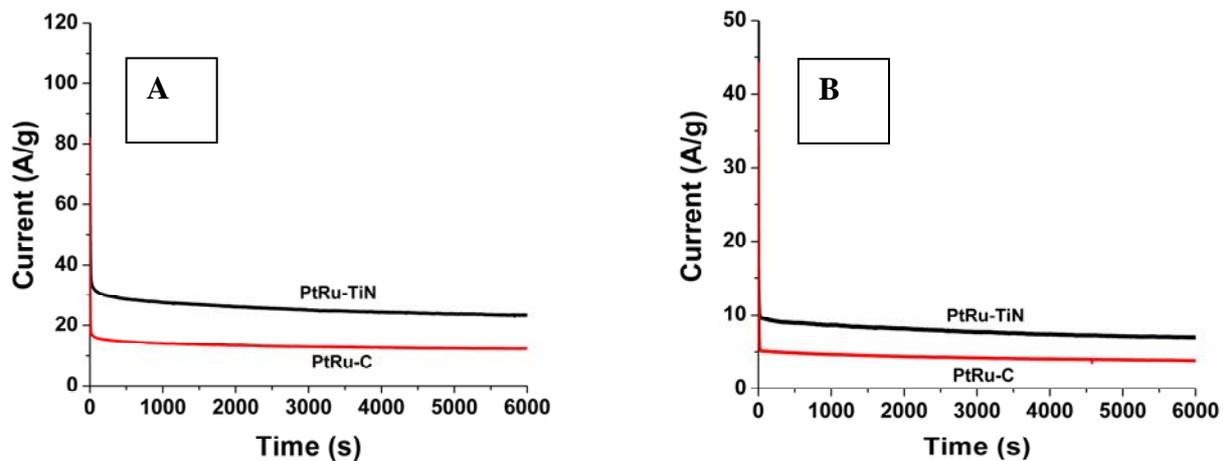


Fig. S12 Current-time transients for PtRu-TiN and PtRu-C catalysts at over potentials of (A) -0.16 V and (B) -0.31 V in 1M KOH containing 0.5M methanol. Loading of catalyst is 1 mg of Pt / cm².

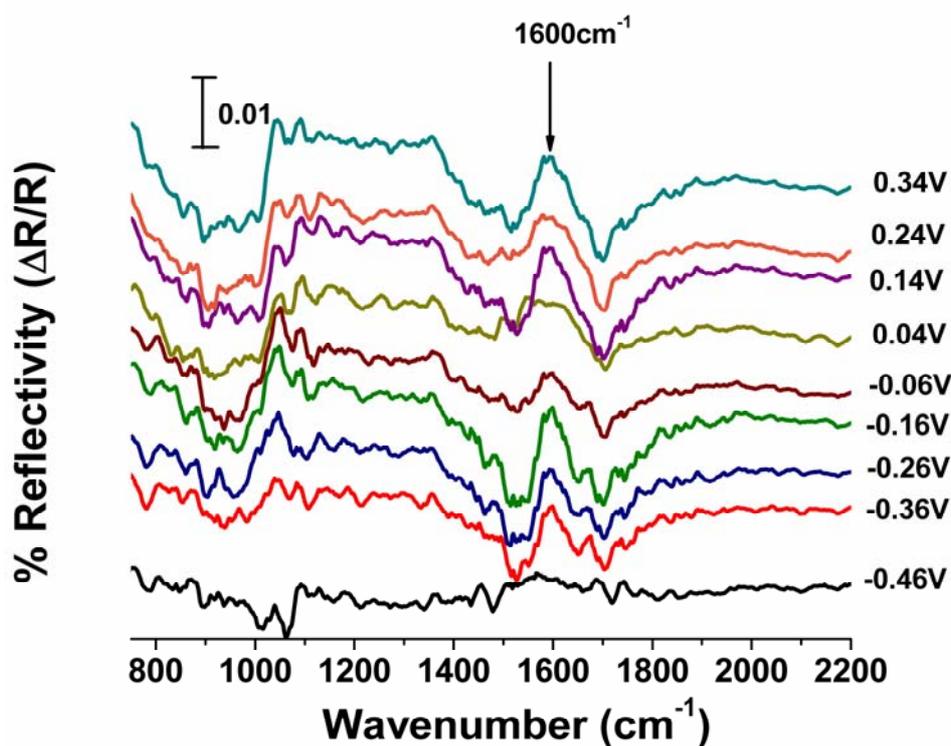


Fig. S13 *In-situ* FTIR spectra in the range, 800 to 2000 cm^{-1} for the electrooxidation of methanol on platinized platinum (Pt-Pt) electrode. Electrolyte used is 0.5M methanol in 1M KOH. The reference spectrum is obtained at -0.56V vs. SHE.